OFFICE OF NAVAL RESEARCH

FINAL REPORT

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CHEMICAL ENGINEERING OF SYNTHESIS SOLUTIONS FOR MULTICOMPONENT INORGANIC POLYMERS AND CERAMICS

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RECENT HIGHLIGHTS OF PROJECT ACCOMPLISHMENTS

Multicomponent Sol to Gel Systems for Coating and Other Applications

While there have been several studies reported in the literature of the structure and properties of organic/inorganic hybrid materials prepared by "sol-gel" chemistry, less is known about how solution conditions influence copolymerization kinetics and material nanostructure. We are developing kinetic polymerization models for structure development of this class of materials. We use ^{29}Si nuclear magnetic resonance spectroscopy to monitor the concentrations of differently hydrolyzed and connected silicon sites, and fit integrated sets of differential equations to these concentrations to quantify kinetic trends as monomers and solution conditions are varied.

Related Work Elsewhere:
R. A. Assink, G. L. Wilkes, J. D. Mackenzie, S. Sakka, H. Schmidt, Y. Sugahara, Z. Zhang, Yamamura Glass Co., Dow Corning, General Electric, Union Carbide, Shin-Etsu Chemical Co.

How Ours is Different:
Models are quantitative and *predictive* ; appropriate simplifications allow us to understand kinetics of large sets of reactions ; we use reaction *transients* to engineer materials. Hydrolysis pseudoequilibrium demonstrated and utilized ; first shell substitution effects on condensation reactivity found for several monomers ; *copolymerization* quantified.

Controlling Precipitation in Sol-to-Gel Coating Systems

The appearance of nanometer scale particles is an important feature in most sol-to-gel reactive coating operations. The size distribution of these particles generally plays a critical role in all performance properties of the coating. We investigate the roles of particle formation and growth steps on the final particle size distribution. Using ^{29}Si NMR, SEM, TEM, conductimetry, and photon correlation microscopy, we monitor the effect of reactor composition on intermediate concentration and

final size distribution. To date we have found that increasing reaction rates sharpens the final size distribution and that a balance between nucleation and growth rates must be struck to achieve self-sharpening growth.

Related Work Elsewhere:
C.F. Zukoski, E. Matijevic, E. Gulari, A. van Blaaderen, S. Kim, A.K. van Helden, C.J. Brinker, D. Ramkrishna, Oak Ridge National Laboratory, Xerox, 3M, PQ, Norton, Toshiba, and Mitsubishi Mining and Cement Co.

How Ours is Different:
Kinetic modeling using ^{29}Si NMR to trace the role of nucleation profile.

Optimization of sol/gel processes by programmed chemical kinetic transients

Given that most sol/gel applications are in coating processes, we design and test chemical kinetic transients to take place after coating in order to regulate the development of molecular architecture and so influence film microstructure and properties. We both: 1) "precondition" the coating fluid so as to provide post-coating kinetic transients and 2) to deliberately manipulate post-coating process parameters that govern kinetics. Liquid and solid state NMR of ^{29}Si and of ^{13}C provides our major means of monitoring chemical kinetics transients and identifying specific molecular architectures, such as small rings and cages.

Related Work Elsewhere:
Union Cabide, Dow Corning, GE, Dow Chemical, Bell Labs, Phillips, 3M, Eastman Kodak, R. A. Assink (Sandia), W.G. Klemperer (U of Illinois), J. Livage (Université Perrie et Marie Curie, France), F. Devreux (Ecole Polytechnique, France), B. Cabane (CNRS, France) J.J. van Beek (U of Utrecht, The Netherlands), H.C. Marsmann (Universität Paderborn, Germany)

How Ours is Different:
The novelty of our approach is in designing deliberately programmed kinetic transients and assembling thermodynamic and kinetic models with no empirical assumptions.

PUBLICATIONS RESULTING FROM THIS PROJECT

Support for this work has been leveraged with several fellowships for graduate student support. These papers include specific acknowledgement of ONR support.

23. "Kinetic and thermodynamic issues in sol-gel processes (polymerization of TEOS in water/ethanol solutions," J. Sefcik and A. V. McCormick, accepted, Catalysis Today, 5/95.
22. "Acidic sol-gel polymerization of TEOS: effect of solution composition on cyclization and bimolecular condensation rater," L. Ng, and A. V. McCormick, accepted Journal of Physical Chemistry, 5/95.
21. "^{51}V NMR of homogeneous multicomponent vanadium oxide solutions," with Kangtaek Lee, Gary Pozarnsky, Odile Zarembowitch, and Alon McCormick, in press Chemical Engineering Journal 4/96.
20. "Hindered diffusion of dextran in chromatographic porous zirconia," C. F. Lorenzano-Porras, M. Fickinger, P. W. Carr and A. V. McCormick, submitted to AIChE Journal, 4/95.
19. "^{51}V NMR Studies of Fast Aqueous Synthesis Methods for V_2O_5 Sols," G. A. Pozarnsky and A. V. McCormick, in press Journal of Materials Science Letters, 4/96.
18. "Thermochemistry of silicate anion precursors to ceramics," J. Sefcik, and A. V. McCormick, submitted to Heterogeneous Chemistry Reviews,5/96.
17. "Effect of composition on the nucleation profile in the synthesis of SiO2 colloids," K. Lee, J. L. Look, M. T. Harris, and A. McCormick, submitted, JCIS, 5/96.
16. "Kinetic investigation into the nucleation mechanism in the synthesis of SiO2 colloids," K. Lee, M. T. Harris, and A. McCormick, submitted, JCIS, 5/96.
15. "Acidic Sol-Gel Polymerization of TEOS: Effect of Solution Composition on Cyclization and Bimolecular Condensation Rates", L. Ng and A. McCormick, in press, J. Phys. Chem., 5/96.
14. "Sol/gel kinetics for the preparation of inorganic/organic siloxane copolymers," S. Rankin, C. W. Macosko, and A. McCormick, in press, Better Ceramics Through Chemistry VII (D. Schaefer et al., eds.), 1996.
13. "The role of transesterification in the multi-step 'prehydrolysis' sol/gel synthesis of aluminum-rich aluminosilicate gels," G. A. Pozarnsky, Kangtaek Lee and Alon McCormick, in press, Journal of Materials Research, 11/95.
12. "^{29}Si-NMR kinetic study of tetraethoxysilane and ethyl-substituted ethoxysilane polymerization in acidic conditions," Jorge Sanchez, Stephen Rankin and Alon McCormick, Industrial and Engineering Chemistry Research, **35**, 1996, 117-129.

11. "Formation of cage-like intermediates from non-random cyclization during acid catalyzed sol-gel polymerization of TEOS," L. V. Ng, P. Thompson, J. Sanchez, and A. V. McCormick, Macromolecules, 28, 1995, 6471-6476.
10. "The role of local bond configuration in the kinetic structure determination of silicate network," with Jorge Sanchez, Ceramic Transactions, (Sol-Gel Science and Technology) ed. Ed Pope, vol. **55**, 1995.
9. "^{17}O NMR spectroscopy of the structural evolution of V_2O_5 gels," G. Pozarnsky, and A. V. McCormick, Journal of Material Chemistry, **4**(11), 1994, 1749-1753.
8. "Multinuclear NMR study of aluminosilicate sol-gel synthesis using the prehydrolysis method," with Gary Pozarnsky, Journal of Non-Crystalline Solids, **190**, 1995, 212-225.
7. "Recent progress in the study of the kinetics of sol/gel SiO_2 synthesis reactions," A. V. McCormick in Sol-Gel Processing and Applications, ed. Yosri Attia, Plenum Science Publishers, 1994, (proceedings of the International Symposium on Sol/Gel Processing, 8/93).
6. "Effects of aging time on V_2O_5 sol/gel coatings," G. Pozarnsky, L. Wright, and A. V. McCormick, Journal of Non-Crystalline Solids, 1994, **3**, (1), 57-62.
5. "^{51}V NMR and EPR study of reaction kinetics and mechanisms in V_2O_5 gelation by ion exchange of sodium metavanadate solutions," G. Pozarnsky, and A. V. McCormick, Chemistry of Materials, 1994, **6** (4), 380-385.
4. "Intramolecular vs. intermolecular condensation rates in the acidic polymerization of octaethoxytrisiloxane," J. Sanchez and A. V. McCormick, Journal of Non-Crystalline Solids **167**, 289-294, 1994.
3. "Transparent aluminosilicate gels fom single alkoxides: current directions," G. Pozarnsky, E. Westenberg, O. Zarembowitch, and A. V. McCormick, Journal of Sol Gel Science, **2**, 7-10 1994.
2. "Preparation of homogeneous aluminosilicate gels by sol-gel methods," M. Reese, J. Sanchez, and A. V. McCormick, in "Synthesis and Processing of Ceramics: Scientific Issues" (W. E. Rhine et al., eds.), MRS Symposium Series **#249**, 1992, p. 69.
1. "Kinetic and thermodynamic study of the hydrolysis of silicon alkoxides in acidic alcohol solutions," J. Sanchez and A. V. McCormick, Journal of Physical Chemistry, **96**, 8973-8979, 1992.

GRADUATE STUDENTS, POSTDOCS, VISITING SCIENTISTS, AND COLLABORATORS

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Gary Pozarnsky - Intermediates in multicomponent sol/gel reactions. Now with Clarkson University, Potsdam, NY.

Jorge Sanchez - Kinetics of SiO2 sol/gel reactions. Now with AT&T Bell Labs, Murray Hill, NJ

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Collaborators

Mike Harris (Oak Ridge National Labs) - sol gel synthesis of particles.

Gary Wieber (Dow Corning) - sol gel synthesis of inorganic/organic hybrid copolymers.